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FULL LENGTH ARTICLE

Hydro-geochemical and isotopic composition of ground water in Helwan area

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Abstract The present study examines the hydro-geochemical and isotopic composition of eight ground water samples at Helwan governorate area in order to identify the main hydro-geochemical processes controlling their chemical content as well as to assessing the quality of these waters. For such purpose of study, many parameters have been analyzed such as pH, electrical conductivity, total dissolved solids (TDS), hardness, major cations and anions. Also, one surface Nile water sample was analyzed and compared with the results of ground water samples. Various water quality classification systems were used to characterize the different ground water types.

The chemical composition of the studied ground water is strongly influenced by the lithology, especially limestone, and dolomitic limestone. The processes contributing the concentrations of major ions depend on carbonate dissolution and cation exchange. Piper diagram showed that bicarbonate is the dominant anion in all the studied ground water samples and the majority of the samples are characterized by mixed cationic composition where no dominant cation is present and thus classified into two water types: Ca–Na–Mg–HCO_3 type and Na–Ca–HCO_3 type. All samples are grouped as Normal-chlorinated, Normal-sulfated, while most samples are grouped as Hyper-carbonated.

The source aquifers of most ground water samples are continuously replenished by fresh samples. This can be verified by studying the genetic systems of the ground water aquifers and most of the ground water samples source in an area of ground water recharge.

The environmental stable isotopes oxygen and hydrogen (^{18}O, and deuterium) were studied and used to identify the sources of recharge. The studied ground waters are enriched in D and ^{18}O and the isotopic features suggest that most of the ground water recharged indirectly after evaporation prior to infiltration from irrigation return water as well as the contribution from Nile water.

1. Introduction

Although Egypt has the great River Nile, which is the main source of water, Egypt's water is limited. Owing to the rapid

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growth of the population and the increasing consumption of water in agriculture, industry, domestic use, etc., Egypt will safeguard its water resources in the future, both with respect to quantity and quality and it will use its resources in the best way from a socio-economic and environmental point of view. It is expected that Egypt will rely to some extent on ground water to develop new projects and to meet the needs of drinking water for future generations [1].

Ground water will be an important source of future water supply and will play a crucial role in any kind of development. Ground water contamination decreases the amount of available useful ground water, especially in the presence of fractures and macro-pores, which can rapidly distribute solutes over a vast area. In the case of fractured aquifers, adventive-dispersive transport is combined with matrix diffusion [2–7].

Ground water in the Helwan area, is an important water resource not only for drinking and agriculture purposes, but also because several famous mineral springs have their origin in the fractured carbonate aquifer in this region [8]. The circulation of spring water through limestone, the biological activity and the presence of CO_2 in the soil are all the reasons responsible for the dissolution of carbonate rocks and generation of some karst feature under the Helwan area [9]. The area is heavily populated with a high density of industrial activities which may pose a risk for ground water and surface water resources. High concentrations of chloride, sulfate, hardness, and significant mineralization were detected under the industrial and high-density urban areas. The presence of shale and marl intercalation within the fissured and cavernous limestone aquifer promotes the exchange reactions and dissolution processes [8].

The environmental isotopes of oxygen-18 (^{18}O) and hydrogen (D) are excellent tracers for determining the origin of ground water and widely used for studying the ground water recharge, migration pathways and mixing of waters from different sources [9–13]. Water isotopes ratios have played a key role in understanding the hydrologic cycle [14–15], hydrologic processes, water movement and distribution, as well as catchment contaminant distribution and transport [16–23].

The main purpose of the present study is to investigate the hydro-geochemical characteristics of ground waters in Helwan area in order to identify the main hydro-geochemical processes controlling their chemical content. A further objective of the study was to assess the quality of these ground waters, for such assessments many more parameters should have been analyzed such as pH, electrical conductivity, total dissolved solids (TDS), hardness, major cations and anions. Various water quality classification systems were used to characterize different ground water types. Piper diagram was used to establish the dominant chemical types of the ground water. Several genetic coefficients and saturation indexes related to the aquifer host rocks and the rocks through which the water passes were determined.

Also, the environmental stable isotopes (oxygen-18, and deuterium) analyses were used to define the source and origin of the ground waters as well as the main recharge sources feeding the ground water wells under study.

2. Studied area

The area under study is located South-East Cairo Fig. 1. It is characterized by low to moderate topography. Some steep slopes are observed behind the factories. The recorded highest elevation is about 60 meters above mean sea level (amsl), while the lowest elevation is about 38 meters (amsl) at the eastern part, the general stratigraphic column of the studied area is as follows from bottom to top [24],

- Observatory formation: it is of Middle Eocene age and consists of white limestone to chalk at some places. Its thickness reaches 80 meters.
- Qurn formation: it is about 70 meters thick of Middle Eocene dolomitic limestone (at the bottom) to white limestone (at the top).
- Wadi Garawi formation: it is conformable with the underlain and overlain formations. Its thickness reaches 50 meters of argillaceous to marly limestone.
- Wadi Houf formation: it is of Upper Eocene age and consists of marl to marly clay.
- Kom El-Shelul formation: it occupies a limited area in the southern part of the studied site and consists mainly of marl, sand and sandy limestone of Pliocene age. The thickness of this formation varies from few meters to about 25 meters.
- Quaternary deposits: they consists mainly of alluvium deposits with a thickness reaching to about 3 meters.

3. Experimental methods and sampling

This study was carried out on eight ground water samples and one surface Nile water sample. The ground water samples were collected by covering the city between El-Tibein and el-Messara at Helwan Governorate (Fig. 1). These samples are given in Table 1. All water samples were subjected to a complete analysis including physico-chemical assessments, different inorganic constituents (anions and cations), and chemical stable isotopes.

3.1. Hydro-chemical characteristics

Hydrochemical characteristics including general physicochemical properties (pH, electrical conductivity, total dissolved solids, and total hardness), major anions (chloride, bicarbonate, sulfate), and major cations (calcium, magnesium, sodium, and potassium) were determined for the water samples. All analyses had been achieved according to the standard test methods [25–27], given in Table 2.

3.2. Environmental chemical stable isotopes

The environmental stable isotopes (oxygen-18 and deuterium) for water samples were measured at the central laboratories for environmental isotopes hydrology at Nasr city, Egypt. The $\delta^{18}O$ values in samples were analyzed via equilibration with CO_2 at 25 °C for 24 h [28]. Both $\delta^{18}O$ and δD values were determined relative to internal standard that were calibrated using IAEA SMOW standards. Data were normalized [29] and are expressed relative to Vienna Standard Mean Ocean Water (VSMOW) in δ units (‰) according to the following equations:

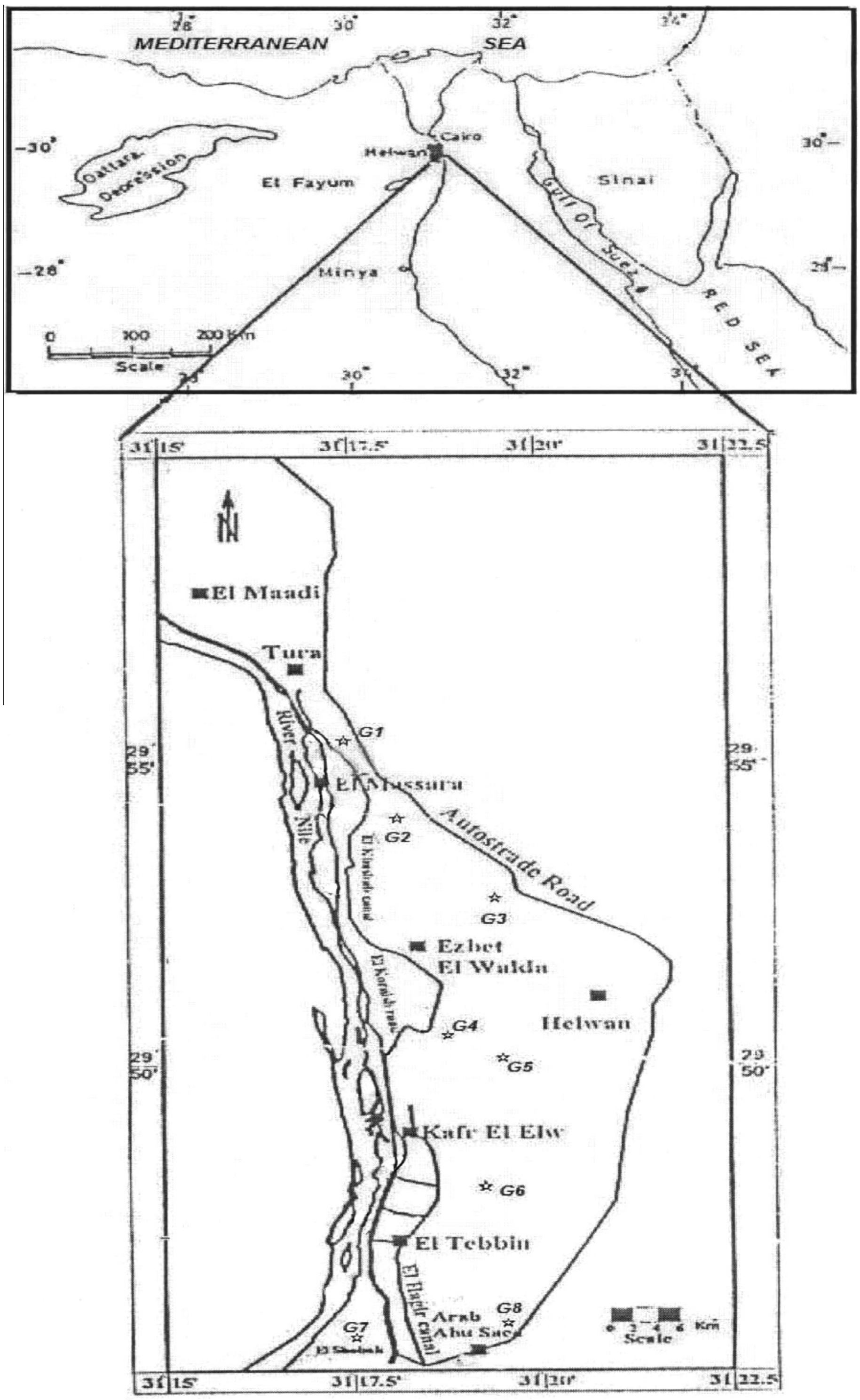

Figure 1 Location map of the studied area. ☆G – ground water samples.

$$\delta^{18}O = [((^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard})]/((^{18}O/^{16}O)_{sample}) \times 10^3\ (\%)$$

$$\delta D = [((D/H)_{sample} - (D/H)_{standard})]/((D/H)_{sample}) \times 10^3\ (\%)$$

where, oxygen and hydrogen isotope ratios are expressed by $\delta^{18}O$ and δD, respectively, $(^{18}O/^{16}O)$ sample or (D/H) sample is the isotopic ratio in the sample water, $(^{18}O/^{16}O)$ or (D/H) is isotopic ratio in standard mean ocean water standards.

Table 1 Location and Bir name of selected samples.

Well name	Water sample No.
El-Massara	G1
El-Badrashin	G2
Abu-Radwan (Aiat Road)	G3
Mazghona (1)	G4
Mazghona (2)	G5
El-Dokomy	G6
Shobak (1) 400 m from Nile	G7
Shobak (2) 600 m from Nile	G8
Nile surface water	S_{Nile}

Table 2 Methods used for the analysis of quality parameters.

Parameters	Methods used
pH	Electrometric method at 25 °C, ASTM D1293 and APHA 4500H+ methods
EC	Digital conductivity meter at 25 °C, ASTM D1125 and APHA 2510 methods
TDS	Drying the suitable aliquots at 180 °C in an oven, ASTM D1888, APHA 2540 C methods
TH	Calculated as calcium carbonate, ASTM D1126 and APHA 2340 B methods
Cl^- and SO_4^{2-}	Ion chromatography, ASTM D4327 and APHA 4110 methods
HCO_3^-	Titration method, ASTM D1067 and D3875 and APHA 2320 methods
Ca^{2+}, Mg^{2+}, Na^+ and K^+	Ion chromatography, International Standard, ISO 14911 method

4. Results and discussion

The hydro-chemical content of the ground water is determined by the composition of the rocks it is abstracted from. Similar types of rocks may lead to different types of mineral water. The chemical content depends on the availability of mineralizing agents, such as CO_2 concentration, redox conditions and the type of adsorption complexes [30]. The hydro-chemical content was used to identify the chemical similarities/differences between the ground water and the fresh surface Nile water.

4.1. Physico-chemical properties

General physico-chemical properties, including pH, electrical conductivity, total dissolved solids, and total hardness were determined for the water samples under study. The results are given in Table 3, together with the guide values GV recommended by WHO (2008) [31] and maximum contaminant levels MCL set by EPA (2009) [32].

The pH of the studied ground water samples at 25 °C varies from 6.87 to 7.90. Minimum pH is observed in sample G8, and maximum pH in G5, indicating nearly neutral to slightly alkaline, while pH of the surface Nile water is higher 8.16 indicating weakly alkaline. A pH value of 6.5 is the minimum recommended by WHO and EPA.

The electrical conductivity (EC) was measured at 25 °C, it varies from 617 μS/cm measured in sample G5 up to 1583 μS/cm measured in sample G7, The maximum permissible values for drinking water is 1400 μS/cm (WHO, 1993) [33] indicating higher EC values and consequently higher total dissolved solids in sample G7. EC of surface Nile water is 451 μS/cm.

Total dissolved solids (TDS) consist of inorganic salts (such as calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates) and small amounts of organic matter that are dissolved in water. TDS of the studied ground water samples determined at 180 °C, are in the range of 554 mg/L to 867 for samples G5, G3, G6, and G4 and in the range of 1013–1389 mg/L for the other samples. TDS of surface Nile water is 372 mg/L. The maximum permissible concentration of TDS for drinking is 1000 mg/L, based on taste considerations (WHO, 1993) [33].

The major portion of the total hardness is caused by calcium and magnesium ions. Total hardness (T.H.) has been estimated from calcium and magnesium concentrations and calculated (as calcium carbonate) from the following equation T.H. = 2.497 Ca + 4.11 Mg. According to Sawyer and McCarthy's [34], hardness is commonly classified in terms of degree of hardness as (1) Soft: Zero → 75 mg/L, (2) Moderate: 75 mg/L → 150 mg/L, (3) Hard: 150 mg/L → 300 mg/L and Very Hard > 300 mg/L. Hardness above approximately 200 mg may cause scales in water pipes and distribution systems. Soft water, with a hardness of less than 100 mg/L may have a low buffering capacity and so be more corrosive for water pipes [35]. Some evidence indicates its role in heart

Table 3 Physico-chemical parameters and the major constituents (in mg/L) of the studied waters.

Water samples	pH	Cond μS/cm	TDS mg/L	Total hardness	Cations mg/L				Anions mg/L		
					Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	Cl^-
G1	7.72	1369	1152	343	204	5.92	61.6	45.9	500	239	95.7
G2	7.78	1175	1013	421	129	8.07	84.4	51.2	470	154	118
G3	7.68	826	803	394	65.1	7.99	98.6	35.8	467	51.0	77.4
G4	7.82	1031	867	392	97.1	7.54	86.0	43.1	421	83.7	128
G5	7.90	617	554	246	60.3	6.43	47.9	30.7	287	60.2	62.1
G6	7.70	885	836	405	65.4	7.34	95.8	40.3	554	3.10	70.4
G7	7.55	1583	1389	500	211	11.9	123	46.7	634	156	206
G8	6.87	1091	1007	459	110	6.75	101	50.2	494	117	128
S_{Nile}	8.16	451	372	158	41.7	5.46	40.6	13.6	188	43.8	39.8
WHO(GV)	6.5–8	–	–	–	–	–	–	–	–	250	250
EPA(MCL)	6.5–8.5	–	500	–	–	–	–	–	–	250	250

disease and unsuitability of hard water for domestic use [36]. Total hardness of the studied ground water samples are in the range of 246 mg/L in samples G5 up to 500 mg/L as in samples G7. Accordingly, sample G5 is considered hard and the other samples are considered very hard while T.H. of surface Nile water is moderately hard 158 mg/L.

4.2. Cations and anions

The concentrations of the major constituents (cations and anions) are determined and the results are given in Table 3. The concentrations of Na^+ range between 60.3 to 129 mg/L, except samples G1 and G7, have concentrations more than 200 mg/L. Concentration of Na^+ ions is 41.7 mg/l in S_{Nile}. The concentration of K^+ was quite low, varying from 5.9 to 11.9 mg/L in ground water samples and is about 5.46 mg/L in S_{Nile} . The concentrations of Ca^{2+} are in the range of 47.9 mg/L in sample G5 to 123.17 mg/L in sample G7 and 40.6 mg/L in S_{Nile}. The concentrations of Mg^{2+} ions are between 30.7 mg/L to 51.2 mg/L in the ground water samples and 13.4 mg/L in S_{Nile}.

The concentrations of Cl^- ions in the studied ground water samples are high reaching up to 206 mg/L, while in S_{Nile}, it is 39.8 mg/l . The concentrations of bicarbonate ions HCO_3^- are more than the chloride ion concentrations, but, have less tolerance value due to original mineral sources [37]. The bicarbonate content varies from 287 mg/L to 634 mg/L in the studied ground water samples and 188 mg/L in S_{Nile}. The concentrations of sulfate ions SO_4^{2-} in all samples are in the range of 51 mg/L and 156 mg/L, except sample G6 that recorded the lowest value of 3.1 mg/L and sample G1 recorded the highest value of 239 mg/L, in S_{Nile} record 44.0 mg/L.

Higher concentration of Ca^{2+} and bicarbonate is observed in samples G6 and G7 because of the abundance of limestone. Calcium readily dissolved from rocks rich in calcium minerals, clay minerals, sulfates and other carbonate rocks especially limestone and gypsum [38].

Concentration of Ca^{2+} was greater than Mg^{2+} in all samples. Concentrations of sodium are high in samples G7 and G1, Primary source of sodium in natural water is from the release of soluble products during the weathering of plagioclase feldspars [38]. No health-based guideline value is proposed for Ca^{2+}, K^+, $Mg^{2+}$and Na^+ in drinking water by WHO due to contrasting views on health impacts of these elements. Each country set its own standards based on its local circumstances.

Chloride (Cl^-) in water comes from sea water entrapped in sediments, solution of halite or chloride contributed by rain. Bicarbonate (HCO_3^-) is the most dominant anion probably because of the reaction of atmospheric and soil carbon dioxide with water and from carbonate dissolution. Sulfate (SO_4^{2-}) in natural water originates from oxidation of sulfide ores, gypsum and anhydrite.

The higher sodium, chloride and sulfate content in sample G1 relative to the others might be resulting from the release of soluble products during weathering of plagioclase feldspars, salt water intrusion or chloride-rich rainwater.

No standards or guideline value is proposed for HCO_3^- in drinking water. The standards/guideline values provided for Cl^- and SO_4^{2-} are based on consumer's acceptability of taste.

4.3. Hydro-geochemical classification of ground water

Different hydro-chemical classification systems have been used to classify water types. The studied water samples are classified according to (i) total dissolved solids (TDS) (ii) dominant ions.

4.3.1. Classification based on TDS and characterizing cations and anions

The European Union (EU) mineral water directive [39] was used to classify water. The criteria for the chemical composition of mineral water according to the EU mineral water directives are given in Table 4. The criteria show a distinction based on TDS and a further specification based on some characterizing cations and anions.

Classification of the ground water in accordance with EU mineral water directive show that all the samples fall in the class "intermediate mineral concentration" (TDS between 500 and 1500 mg/L). Based on the characterizing cations and anions, Sample G7 falls in class containing bicarbonate with bicarbonate > 600 mg/L, also, it falls in class containing chloride with chloride > 200 mg/L, and in class containing sodium with sodium > 200 mg/L, sample G1 falls in class containing sulfate and in class containing sodium, G2 and G8 fall in class containing magnesium with magnesium > 50 mg/L.

Table 4 Mineral water classification based on EU directive.

Mineral water type	Criterion
Very low mineral concentration	Mineral content (TDS) < 50 mg/L
Low mineral concentration	TDS 50–500 mg/L
Intermediate mineral concentration	TDS 500–1500 mg/L
High mineral concentration	TDS > 1500 mg/L
Containing bicarbonate	Bicarbonate > 600 mg/L
Containing sulfate	Sulfate > 200 mg/L
Containing chloride	Chloride > 200 mg/L
Containing calcium	Calcium > 150 mg/L
Containing magnesium	Magnesium > 50 mg/L
Containing sodium	Sodium > 200 mg/L
Suitable for low sodium diets	Sodium < 20 mg/L

Table 5 Concentrations of major constituents (in meq/l) for the studied water samples.

Water samples	Cations meq/L				Anions meq/L		
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	Cl^-
G1	8.87	0.15	3.08	3.78	8.20	4.98	2.70
G2	5.61	0.21	4.21	4.21	7.70	3.21	3.33
G3	2.83	0.20	4.92	2.95	7.66	1.06	2.18
G4	4.22	0.19	4.29	3.55	6.90	1.74	3.61
G5	2.62	0.16	2.39	2.53	4.70	1.25	1.75
G6	2.85	0.19	4.78	3.32	9.08	0.07	1.99
G7	9.17	0.30	6.14	3.84	10.39	3.25	5.81
G8	4.79	0.17	5.05	4.13	8.10	2.44	3.60
S_{Nile}	1.82	0.14	2.03	1.12	3.08	0.91	1.12

Table 6 Classification of the studied water samples.

Water samples	Chlorinated type	Sulfated group	Bicarbonated group	Saturation with $CaSO_4$ $\sqrt{(SO_4)(Ca)}$		Saturation with $CaCO_3$ $\sqrt[3]{(HCO_3+CO_3)^2(Ca)}$	
G1	Normal	Normal	Hyper	3.91	Under Sat.	5.91	Under Sat.
G2	Normal	Normal	Hyper	3.67	Under Sat.	6.26	Under Sat.
G3	Normal	Normal	Hyper	2.29	Under Sat.	6.61	Under Sat.
G4	Normal	Normal	Normal	2.74	Under Sat.	5.89	Under Sat.
G5	Normal	Normal	Normal	1.73	Under Sat.	3.75	Under Sat.
G6	Normal	Normal	Hyper	0.56	Under Sat.	7.33	Near Sat.
G7	Normal	Normal	Hyper	4.47	Under Sat.	8.73	Near Sat.
G8	Normal	Normal	Hyper	3.51	Under Sat.	6.92	Under Sat.
S_{Nile}	Normal	Normal	Normal	1.36	Under Sat.	2.68	Under Sat.

4.3.2. Classification based on dominant ions

The studied water samples are classified based on the dominant ions [40–43] and the results are given in Table 6, the concentration of anions and cations are calculated in milliequivalent per litre (meq/L) given in Table 5.

The results show that all samples are grouped as Normal-chlorinated, as they have Cl^- concentrations less than 10 meq/L and are grouped as Normal-sulfated as they have sulfate concentration less than 6 meq/L. On the other hand, two samples G4, G5, and S_{Nile} are Normal-carbonated as they have bicarbonate concentrations in the range 7 – 2 meq/L, and the other samples are grouped as Hyper-carbonated as they have bicarbonate greater than 7 meq/l.

The saturation index with calcium sulfate, $\sqrt{(SO_4)(Ca)}$, indicates that all samples are under saturated, as they have $\sqrt{(SO_4)(Ca)}$ values less than 70. The saturation index with calcium carbonate, $\sqrt{(HCO_3+CO_3)^2(Ca)}$, indicates that all samples are under saturation, as they have values less than 7 meq/L, except samples G6, and G7 are near saturation, as have values greater than 7 meq/L.

4.4. Representation of the studied water samples graphically

The ground water samples are represented graphically using pie diagram [44] and Piper's diagrams [45]. Pie charts and Piper's diagram were drawn using the relative proportion of major ions in each ground water sample in % meq/L.

4.4.1. Pie diagrams

Fig. 2 shows the relative proportion of major ions in each ground water sample in % meq/L. The concentrations of cations of the studied water samples are ordered from higher to lower as $Na^+ + K^+ > Mg^{2+} > Ca^{2+}$ in samples G1 and G5, as $Ca^{2+} > Na^+ + K^+ > Mg^{2+}$ in samples G3, G8, and S_{Nile} , as $Na^+ + K^+ > Ca^{2+} > Mg^{2+}$ in samples G2, G4, and G7, and as $Ca^{2+} > Mg^{2+} > Na^+ + K^+$ in sample G6. The concentrations of anions in all studied water samples follow the order $HCO_3^- > Cl^- > SO_4^{2-}$.

Pia diagrams show that concentrations of alkalies (Na + K) exceed the concentration of alkaline earth (Ca + Mg) in sample G1, while concentrations of alkaline earth exceed alkalies in all other samples from G2 to G8 and S_{Nile}. Weak acids (HCO_3) exceed strong acids (Cl + SO_4) for all ground water samples and S_{Nile} water.

4.4.2. Piper diagram

On this diagram the relative concentrations in % meq/L of the major ions were plotted on two separate cations and anions triangles, and then the locations were projected to a point on a diamond quadrilateral plot where the points from the linear plots of cations and anions are projected to indicate the character of the water by the relationships among the Na + K, Ca + Mg, CO_3 + HCO_3, Cl + SO_4, ions and give a specific ground water type.

The studied water samples were classified into water types using Piper diagram (Fig. 3). As indicated the majority of ground water samples (G2 to G8) are characterized by mixed cationic composition where no dominant cation present, while ground water sample G1 is Na–K cationic composition. All samples are characterized with anionic composition dominated by bicarbonates. Thus the water samples are classified into two water types: Samples G2 to G8 and S_{Nile} water belong to Ca–Na–Mg–HCO_3 type, while sample G1 belongs to Na–Ca–HCO_3.

4.5. General geochemistry of the source of the studied ground water samples

Concentration ratios, expressed in meq/L, of a certain ion in relation to another take values that are related to (a) the aquifer host rocks, or (b) the rocks through which the water passes, or (c) the degree of replenishment of ground water, or (d) its mixing with sea water [46,47]. Various ion relationships including Mg^{2+}/Ca^{2+}, Na^+/Cl^-, Na^+/K^+, Cl^-/SO_4^{2-}, $(Ca^{2+}+Mg^{2+})/(K^++Na^+)$, Cl^-/Σ anion Cl^-/Σ anions are calculated and the results are given in Table 7.

4.5.1. Various ion relationships

(a) Mg^{2+}/Ca^{2+} ratios denote that the source of ground water is derived from Mg-rich rocks or calcium carbonate lithologies; $Mg^{2+}/Ca^{2+} > 0.9$ aquifers with silicate rich rocks in Mg; Samples G1, G2, and G5 belong to this category as they have $Mg^{2+}/Ca^{2+} > 0.9$; Mg^{2+}/Ca^{2+} = 0.7–0.9 aquifers in dolomitic rocks: Samples G4, and G8 fall in this category; Mg^{2+}/Ca^{2+} = 0.5 – 0.7, aquifers in limestone or carbonate lithology: Samples G3, G6, and G7 belong to this category.
(b) Na^+/Cl^- ratios indicate sources of salinity during ground water flow [48], $Na^+/Cl^- > 1.0$ aquifers in alkaline or metamorphic rocks, exchange of Ca^{2+} and

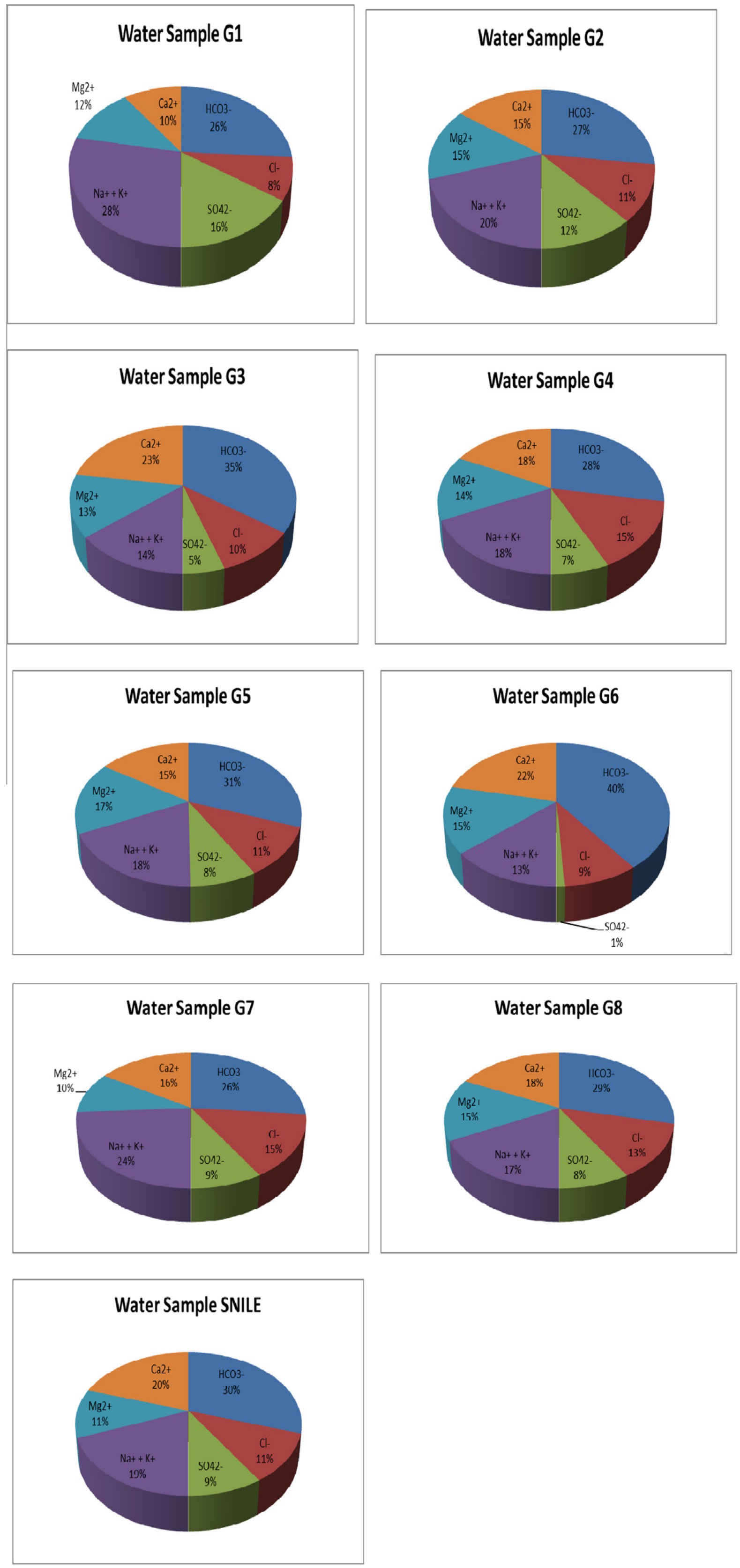

Figure 2 Pia diagrams representation of the major ion concentrations in the studied water samples.

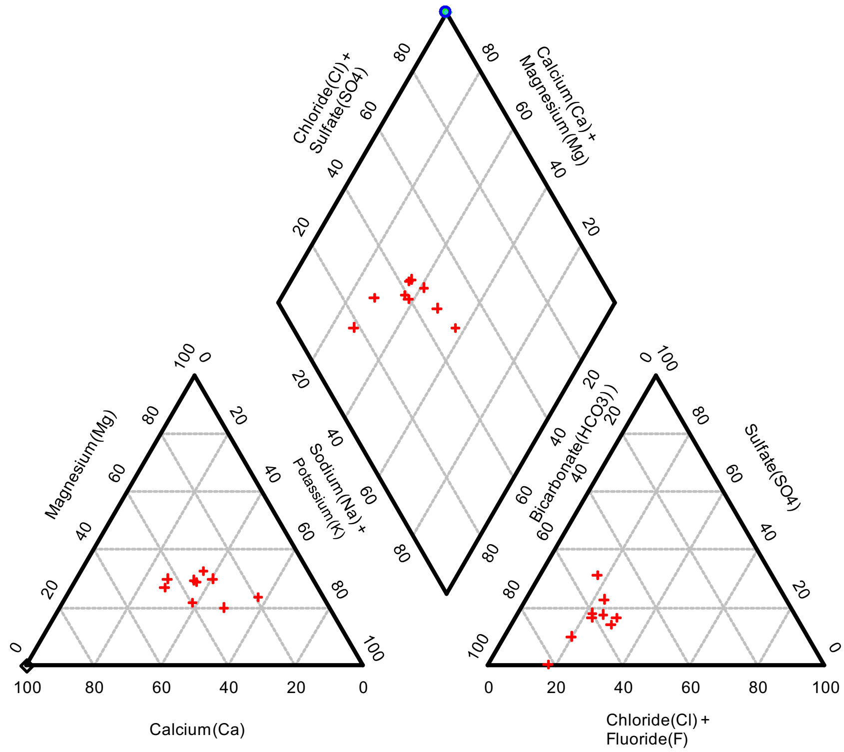

Figure 3 Piper's diagram representation of the studied water samples.

Table 7 Various ion relationships of the major ions in the studied water samples.

Water samples	Genetic coefficients					$Cl^-/\sum$ anions
	Mg^{2+}/Ca^{2+}	Na^+/Cl^-	Na^+/K^+	Cl^-/SO_4^{2-}	$Mg^{2+} + Ca^{2+}/Na^+ + K^+$	
G1	1.23	3.29	59.1	0.54	0.76	0.17
G2	1.00	1.68	26.7	1.04	1.45	0.23
G3	0.60	1.30	14.2	2.06	2.60	0.20
G4	0.83	1.17	22.2	2.07	1.78	0.30
G5	1.06	1.50	16.4	1.40	1.75	0.23
G6	0.69	1.43	15.0	28.4	2.66	0.18
G7	0.62	1.58	29.6	1.78	1.05	0.30
G8	0.82	1.33	28.2	1.48	1.85	0.25
S_{Nile}	0.55	1.63	13	1.23	1.61	0.22

Mg^{2+} by Na^+, All samples have Na^+/Cl^- ratio more than one. The high sodium concentration in ground water indicates addition of sodium through the dissolution and ion exchange processes which withdraws Ca and gives Na to the solution.

(c) Na^+/K^+ ratios are related to whether the source water is affected by sea or rain water, or is derived from an area of ground water recharge: Na^+/K^+ = 50–70 ground water source at the down dip of the aquifer due to adsorption of Na: sample G1 belongs to this category. $Na^+/K^+ \approx 47$ sea water: No samples belong to this category. $Na^+/K^+ = 15 - 30$ ground water source in an area of ground water recharge: All samples from G2 to G8 belong to this category indicating that the studied ground water sources is Nile water and irrigation return water. $Na^+/K^+ \leqslant 10$ rain water: No samples.

(d) Cl^-/SO_4^{2-} ratios are associated with salinization and occurrence of residual salts in the aquifers: $Cl^-/SO_4^{2-} = 5 - 10$ chloride-rich water: Sample G6 fall in this category; $Cl^-/SO_4^{2-} = 1 - 5$ water rich in chloride and sulfate: Samples G2, G3, G4, G5, G7, and G8 belong to this category where the sulfate may be derived from the dissolution of gypsum or anhydrite; $Cl^-/SO_4^{2-} = 0.2 - 1.0$ water rich in sulfate–chloride: sample G1 fall in this category.

(e) $(Ca^{2+} + Mg^{2+})/(K^+ + Na^+)$ ratios: $(Ca^{2+} + Mg^{2+})/(K^+ + Na^+) > 1.0$, aquifer with a continuous recharge: all ground water samples are in this category except sample G1. The $(Ca^{2+} + Mg^{2+})/(K^+ + Na^+)$ ratios suggest that the source aquifers of ground water samples are shallow, and continuously replenished by fresh water. This observation is verified by the Na^+/K^+ ratios, most of which have values of < 50.

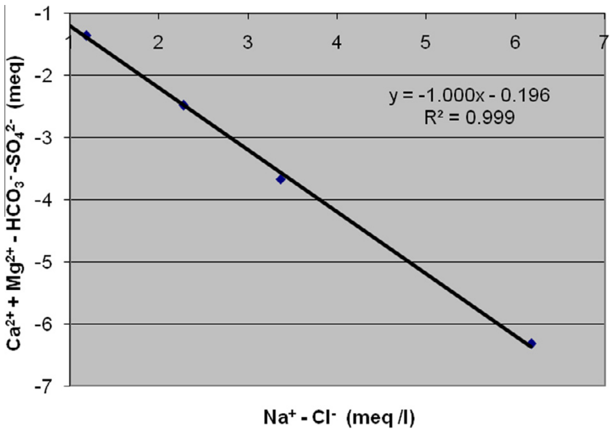

Figure 4 Plot of ($Na^+ - Cl^-$) versus ($Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$) for the studied ground water samples.

(f) Cl^-/Σ anion ratios: The studied ground water samples have Cl^-/Σ anion ratios varying from 0.17 to 0.30. Since, Cl^-/Σ anion ratios are <0.8, the ground water sources are not seriously affected by dissolution of halite or other evaporitic minerals, and sites not affected by sea water intrusion.

(g) Evidence of ion exchange is provided by the ($Na^+ - Cl^-$) versus ($Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$) diagram [49,50] (Fig. 4). The ground water samples plot approximately along a line with a slope of −1.00, suggesting that some ion exchange is taking place, as it has been already noted in the description of Na^+/Cl^- ratios.

5. Statistical correlation of analysis

Correlations among all possible pairs of variables of the studied ground water samples have been performed using the linear regression analysis and the results of the correlation coefficients (r) are given in Table 8.

Correlation coefficients values r show that there is strong positive correlation ($r > 0.8$) between Na^+ and SO_4^{2-}, K^+ and Cl^-, $Ca^{2+}$and HCO_3^-, this indicates that these salts are predominant in most samples. Cl^- shows positive correlation (r = 0.6243 to 0.8016) with Na^+, K^+, Mg^{2+}, and Ca^{2+}, this may be due to the presence of these metals as chloride in some ground water samples. Moderate positive correlation (r = 0.6351–0.5876) between Na^+ and HCO_3^-, K^+ and HCO_3^-, Mg^{2+} and SO_4^{2-} , Mg^{2+} and HCO_3^-, indicates that these salts are present in some ground water samples. Also shown, minor positive correlation between Na^+ and K^+, Mg^{2+} and Ca^{2+}, Cl^- and HCO_3^-, little positive correlation between K^+ and Mg^{2+} , Na^+ and Ca^{2+} , HCO_3^- and SO_4^{2-}, Ca^{2+} and SO_4^{2-} and no-correlation between K^+ and SO_4^{2-}.

Table 8 Correlation among major constituents of the studied ground water samples.

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-
K^+	0.423					
Mg^{2+}	0.619	0.233				
Ca^{2+}	0.224	0.768	0.439			
Cl^-	0.705	0.802	0.624	0.677		
HCO_3^-	0.588	0.635	0.583	0.807	0.624	
SO_4^{2-}	0.889	0.066	0.617	0.103	0.461	0.256

6. Recharge origin of the studied ground waters samples

The water isotopes, which include the stable isotopes of oxygen ($^{18}O/^{16}O$) and hydrogen (D/H), were used in this study to determine the origin of waters, and to identify and quantify geochemical processes that control the chemical composition of ground water. Also, useful information on processes related to water cycling and water–rock interaction can be estimated, that may affect water quality.

The environmental isotopic composition results of the studied ground water samples are shown in Table 9, together with the values of the recent Nile water sample and irrigation return water. The results show that the $\delta^{18}O$ values are in the range of 2.08‰ in sample No. 2 to 4.01‰ in sample No. 8 and δD values are in the range of 16.3‰ in sample No. 2 to 29.06‰ in sample No. 6. The environmental isotopic compositions of the recent Nile water are about 3.36‰ for $\delta^{18}O$ and 24.4‰ for D, and the irrigation return water ($\delta^{18}O$ = 5.3‰ and δD = 39.1‰) [51].

Table 9 The isotopic composition of the studied water samples.

Samples Nos.	Ground water samples	
	δO-18	δD
G1	3.21	20.34
G2	2.08	16.3
G3	3.06	22.68
G4	2.98	26.32
G5	3.11	28.17
G6	3.28	29.06
G7	2.67	24.38
G8	4.01	27.21
Nile water	3.36	24.4
Irrigation return water	5.3	39.1

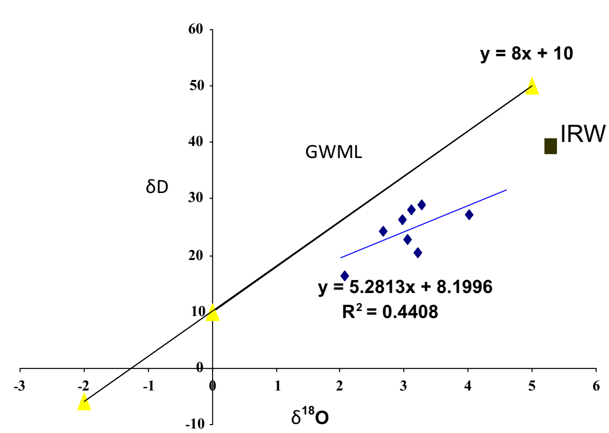

Figure 5 Relationship between $\delta^{18}O$ and δD for the studied ground water samples.

In order to determine the recharge origin of the studied ground water samples, the relationship between δD against $\delta^{18}O$ was drawn (Fig. 5) relative to the Global Meteoric Water line (GMWL) [52] which follows the empirical equation; $\delta D = 8\ \delta^{18}O + 10$, defined by [14] and the Local Meteoric Water Line which represent the local climatic condition of the region (LMWL) follows the empirical equation ($\delta D = 8\ \delta^{18}O + 22$).

The scatter plot for our data set gives a regression line of equation $\delta D = 5.28\ \delta^{18}O + 8.2$, deviation from the meteoric line reflects an evaporation enrichment of heavier isotope concentrations has occurred prior to recharge processes. Also, the results reflect that the studied ground water is a mixing contribution from both sources of irrigation return water as well as Nile surface water effect.

7. Conclusions

The chemical composition of the studied ground water is strongly influenced by lithology, especially limestone, and dolomitic limestone. The processes contributing to the concentration of major ions depend on carbonate dissolution and cation exchange. This appears from the following results:

(1) Bicarbonate (HCO_3^- is the most dominant anion in all samples; higher concentration of Ca^{2+} and bicarbonate was observed in samples G6 and G7 because of the abundance of limestone and dissolution of calcium from carbonate rocks especially limestone; concentration of Ca^{2+} is greater than Mg^{2+} in all samples.
(2) All the samples fall in the class "intermediate mineral concentration" based on TDS. Based on the characterizing cations and anions, sample G7 falls in class containing bicarbonate, chloride and sodium; sample G1 falls in class containing sulfate, and sodium; samples G2 and G8 fall in class containing magnesium.
(3) All samples are grouped as Normal-chlorinated, Normal-sulfated, while grouped as Hyper-carbonated except samples G4, G5, and S_{Nile} which are grouped as Normal-carbonated.
(4) All samples are under saturation with respect to gypsum observed from the values of saturation index calcium sulfate, $\sqrt{(SO_4)(Ca)}$. The saturation index with calcium carbonate, $\sqrt{(HCO_3 + CO_3)^2(Ca)}$, indicates that all samples are under saturation, except samples G6, and G7 are near saturation.
(5) The concentration of alkalies (Na + K) exceeds the concentration of alkaline earth (Ca + Mg) in sample G1, while concentrations of alkaline earth exceed alkalies in all other samples from G2 to G8 and S_{Nile}. Weak acids (HCO_3) exceed strong acids ($Cl + SO_4$) for all ground water samples and S_{Nile} water.
(6) The studied water samples are classified into two water types: samples G2 to G8 and S_{Nile} water belong to Ca–Na–Mg–HCO_3 type, while sample G1 belongs to Na–Ca–HCO_3, as indicated from piper's diagram that the majority of ground water samples (G2 to G8) are characterized by mixed cationic composition where no dominant cation present, while ground water sample G1 is Na–K cationic composition and all samples are characterized with anionic composition dominated by bicarbonates.
(7) The source aquifers of the ground water samples are continuously replenished with fresh water for all samples from G2 to G8, this observation is verified by $(Ca^{2+} + Mg^{2+})/(K^+ + Na^+)$ and Na^+/K^+ ratios, most of the ground water source is in an area of ground water recharge, indicating that the studied ground water sources are Nile water and the irrigation return water. Ground water G1 at the down dip of the aquifer is due to the adsorption of Na. The high sodium concentration in most ground water samples indicates addition of sodium is taking place through ion exchange processes which played an important role in the ground water mineralization and withdraws Ca and gives Na to the solution.
(8) Multivariate statistical analysis clarified strong positive relationships ($r > 0.8$) between Na^+ and SO_4^{2-}, K^+ and Cl^-, Ca^{2+} and HCO_3^-, this indicates that these salts are predominant in most samples.
(9) Stable water isotopes (δD and $\delta^{18}O$) have established that an evaporation enrichment of heavier isotope concentrations has occurred prior to recharge processes and the recharge origin of the studied ground water is a mixing contribution from both sources of irrigation return water as well as Nile surface water effect.

References

[1] M.R. El Tahlawi, A.A. Farrag, S.S. Ahmed, Environ. Geol. 55 (2008) 639–652.
[2] R. Baumle, H. Hotzl, K. Witthuser, in: A. Dassargues (Ed.), Tracers and Modelling in Hydrogeology, 262, IAHS Press, Wallingford UK, 2000, pp. 283–288.
[3] R. Baumle, Geohydraulic characterisation of fractured rock flow regimes. Regional studies in granite (Lindau, Black Forest, Germany) and Dolomite (Tsumeb Aquifers, Northern Namibia) (Ph.D. thesis), Department of Applied Geology, Karlsruhe, Germany, 2003.
[4] K. Witthuser, B. Reichert, H. Hotzl, Ground Water 41 (2003) 806–815.
[5] J. Bodin, F. Delay, G. de Marsily, J. Hydrogeol. 11 (2003) 418–433.
[6] J. Bodin, F. Delay, G. de Marsily, J. Hydrogeol. 11 (2003) 434–454.
[7] F.A. Abdalla, Contaminant transport in fractured chalk aquifer characterized by tracer techniques at Sigerslev, Denmark (Ph.D. thesis), Bonn University, Germany, 2004.
[8] Fathy A. Abdalla, Traugott Scheytt, J. Earth Syst. Sci. 121 (1) (February 2012) 109–124.
[9] R. Said, Bull. Soc. Geogr. Egypt 27 (1954) 93–100.
[10] G. Faure, Principles of Isotope Geology, Wiley, New York, 1986.
[11] L.A. Sacks, A.B. Tihansky, US Geol. Surv. Water-Resour. Invest. Rep. (1996) 96–4146.
[12] A.M. Subyani, Environ. Geol. 46 (6) (2004) 741–749.
[13] Younes Hamed, Ferid Dhahri, J. Afr. Earth Sci. 83 (2013) 10–24.
[14] H. Craig, Science 133 (1961) 1702–1703.
[15] W. Dansgaard, Tellus 4 (1964) 436–468.
[16] T. Dincer, Water Resour. Res. 4 (1968) 1289–1306.
[17] P. Maloszewski, A. Zuber, J. Hydrol. 57 (1982) 207–231.

[18] A. Davis, D. Ashenberg, Appl. Geochem. 44 (1989) 23–36.
[19] C. Kendall, J.J. McDonnell (Eds.), Isotope Tracers in Catchment Hydrology, Elsevier, Amsterdam, 1998.
[20] I.J. Winograd, A.C. Riggs, T.B. Coplen, Hydrogeol. J. 6 (1998) 77–93.
[21] K.J. McGuire, D.R. DeWalle, W.J. Gburek, J. Hydrol. 261 (2002) 132–149.
[22] B.D. Smerdon, D.M. Allen, S.E. Grasby, M.A. Berg, J. Hydrol. 365 (2009) 156–172.
[23] Pu. Tao, Yuanqing. He, Tao. Zhang, Wu. Jinkui, Guofeng. Zhu, Li. Chang, Appl. Geochem. 33 (2013) 199–212.
[24] M.G. El-Behiry, S.M. Hanafy, S.T. El-Hemamy, E.G.S. Proc. Of the 17th Ann. Meet. (1999) 145–158.
[25] Annual Book of American Standard Test Method (ASTM), Vols. 11.01 and 11.02, Am. Soc. Test. Mater., Philadelphia, 1992.
[26] APHA, A.D. Eaton, L.S. Clesceri, A.E. Greenberg, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, AWWA, WPCF, New York, 1999.
[27] International Standard, ISO 14911, Determination of Dissolved Li^+, Na^+, NH_4^+, K^+, Mn_2^+, Ca_2^+, Mg_2^+, Sr_2^+ and Ba_2^+ using Ion Chromatography-Method for Water and Waste Water, First ed., 10-01, 1998.
[28] S. Epstein, T.K. Mayeda, Geochim. Cosmochim. Acta 4 (1953) 213–224.
[29] T.B. Coplen, Chem. Geol. 72 (1988) 293–297.
[30] M. Birke, A. Demetriades, B. De Vivo, J. Geochem. Explor. 107 (3) (2010) 217–226.
[31] WHO, Guidelines for Drinking water Quality: Third Edition Incorporating the First and Second Addenda Vol 1 Recommendations, World Health Organization, WHO, Geneva, 2008, 668.
[32] Environmental Protection Agency (EPA), National primary/secondary drinking regulations. EPA816-F-09-004, <http://www.epa.gov/safewater/contaminants>, 2009.
[33] WHO, Guidelines for Drinking Water Quality, Recommendations, vol. 1, World Health Organization, Geneva, 1993, p. 130.
[34] G.N. Sawyer, D.L. McCarthy, Chemistry of Sanitary Engineers, second ed., McGraw Hill, New York, 1967, p. 518.
[35] Z. Jamshidzadeh, S.A. Mirbagheri, Desalination 270 (2011) 23–30.
[36] H.A. Schroeder, J. Chron. Dis. 12 (1960) 586–591.
[37] Siamak Gholami, S. Srikantaswamy, World Appl. Sci. J. 6 (8) (2009) 1157–1169.
[38] Stephanie Abonoje Oyebog, Andrew Ako Ako, George Elambo Nkeng, Emmanuel Cheo Suh, J. Geochem. Explor. 112 (2012) 118–130.
[39] N.G.F.M. Van der Aa, Environ. Geol. 44 (2003) 554–563.
[40] G. Matthess, Die Beschaffenheit des Grundwassers – Lehrbuch der Hydrologie, Band 2, third ed., Borntraeger, Berlin, Stuttgart, 1994, p. 499 (in German).
[41] G. Matthess, K. Ubell, Allgemeine Hydrogeologie – Grundwasserhaushalt Lehrbuch der Hydrogeologie, Band 1, Borntraeger, Berlin, Stuttgart, 1983, p. 438 (in German).
[42] G. Matthess, The Properties of Ground Water, first ed., John Wiley & Sons, New York, 1982.
[43] Klimentov, P., General Hydrogeology, first ed., Russian eds., Moscow, 1983.
[44] Hem, J.D., Study and Interpretation of the Chemical Characteristics of Natural Waters, U. S. Geol. Surv. Water Supply Paper, No. 1473 (1959).
[45] Piper, A.M., 1944, A graphic procedure in the geochemical interpretation of water analyses. American Geophysical Union Transactions 25, 914–923. U.S. Geol. Surv. Ground Water Note No. 12 (1953).
[46] S. Mandel, Z. Shiftan, Groundwater Resources, Investigation and Development, Academic Press, N.Y., London, 1981, p. 269.
[47] Alecos. Demetriades, J. Geochem. Explor. 107 (2010) 283–298.
[48] I. Cartwright, T.R. Weaver, Hydrogeol. J. 13 (2005) 752–770.
[49] J. Jankowski, R.I. Acworth, S. Shekarforoush, in: G.B. Arehart, J.R. Hulston (Eds.), Proceedings of 9th International Symposium of Water-Rock Interaction, Taupo, New Zealand, 30 March–3 April 1998, Balkema, Rotterdam, 1998, pp. 243–246.
[50] B.K. Kortatsi, Environ. Geol. 50 (2006) 299–311.
[51] Salem W. M., (Ph.D. thesis), Faculty of Engineering, Cairo University, 1996.
[52] International Atomic Energy Agency, IAEA, Draft Safety Report, Working document, limited distribution, version 3.0 March, 1999.